

Relativistic equation-of-motion coupled-cluster method for the electron attachment problem

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Abstract

The article considers the successful implementation of relativistic equation-of-motion coupled cluster method for the electron attachment problem (EA-EOMCC) at the level of single- and double- excitation approximation. The implemented relativistic EA-EOMCC method is employed to calculate ionization potential values of alkali metal atoms (Li, Na, K, Rb, Cs, Fr) and the vertical electron affinity values of LiX (X=H, F, Cl, Br), NaY (Y=H, F, Cl) starting from their closed-shell configuration. Both four-component and exact two component calculations are done for all the opted systems. Further, we have shown the effect of spin-orbit interaction considering the atomic systems. The results of our atomic calculations are compared with the values from the NIST database and the results are found to be very accurate ($< 1\%$).

Keywords: *Four-component, EOMCC, Electron affinity, X2C*

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1. Introduction

A considerable growing interest is noticed in recent years in the study of negative ions as negative ions have significance in many areas of physics like in astrophysics, plasma physics and surface physics [1, 2, 3, 4]. The electron affinity (EA) is an important quantity of these ions. The precise measurement of EA of atomic or molecular systems is always a challenge as the resulting negative ion is difficult to handle. Despite of the complexity in the measurement, there have been significant advances in the experimental techniques like laser photodetachment electron spectroscopy (LPES), laser photodetachment threshold spectroscopy (LPTS), accelerator mass spectroscopy (AMS) and photodetachment microscopy, et cetera that are capable of precise measurements of EA of an atomic system [5, 6, 7, 8]. However, the situation is inappreciative in achieving such an extent of accuracy in the molecular systems due to the possibility of structural change on attachment of an extra electron. Therefore, it is an outstanding challenge for the computational physicists to complement these atomic measurements as well as for new predictions for the future purpose.

The computational prediction of EA is difficult due to the absence of long-range Coulomb field outside of a neutral precursor. Therefore, an extra electron is solely bound through correlation with other electrons [9, 10]. Moreover, most of the theoretical calculations are based on the quantum chemical basis set methods. Thus, the finite size of the basis and unbalanced treatment of electron correlation in the atomic or molecular system and in the resulting ion are the sources of error [11, 12]. The attachment and detachment of an electron to a neutral species involves different forces. The attached extra electron to the neutral atom polarizes the electronic shell of the atom. As a result a dipolar electric field is generated which binds the extra electron with the other electrons. The charge distribution of the electron cloud, particularly the electron-electron correlation effects decides the stability of the negative ion. These interactions do not play much role in most of the neutral atoms as well as in positive ions where direct electrostatic force is the dominant factor for the stability of the neutral atom or the positive ion. On the other hand, these effects dominate in the negative ions. Therefore, the calculations of EA values of both atomic and molecular systems are challenging

and is a real test for the performance of a many-body method. It is an established fact that not only the electron correlation but also the effect of relativity play a definite role in accurate description of the eigenstates of heavy atomic and molecular systems [13]. It is, therefore, in such a case a highly correlated many-body method, capable of simultaneous treatment of relativity and electron correlation is required due to the intricate coupling between these two effects [14, 15, 16].

The relativity has a greater role towards the core orbitals and practically important for all the elements. The effects of relativity are incorporated in the electronic structure calculations by the choice of the Hamiltonian. The consideration of Dirac-Coulomb-Breit Hamiltonian without the quantum electrodynamics effects (QED) is sufficient for most of the relativistic electronic structure calculations using four-component wavefunction. However, in actual practice the Dirac-Coulomb Hamiltonian is most commonly used where two-body Coulomb interaction operator is added to the Dirac Hamiltonian (\hat{H}_D). Although, the form of the Coulomb operator is same as in the non-relativistic theory, however, the physical content is different as it takes care of the spin-same orbit interaction. This type of truncation in the two-body interaction does not effect much for most of the chemical purposes [17]. However, for very accurate studies of molecular spectra including fine structure, the inclusion of spin-other-orbit interaction and spin-spin interaction are required which can be done with the full inclusion of the Breit part of the two-body interaction. The relativistic calculations using four-component wave function are very expensive from the computational perspective. A lot of effort has been made to simplify the equations. The calculation of the small component of the wave function is the most challenging part of the computation. If a basis set is expressed in terms of contracted Gaussian functions, then the number of required primitive Gaussian functions for the small component is about twice the number of the large component with the imposition of the kinetic balance condition. On the other hand, the small component has a very minor contribution in the calculated values; therefore, it makes sense to look for an approximation. There are a number of Hamiltonians in between the scalar non-relativistic and four-component relativistic ones. However, the inclusion of the spin-orbit interaction requires at least a two-component description, though it will essentially increase the computational cost

due to the appearance of complex algebra in place of real algebra. The electron correlation methods in the no-pair approximation require the transformation of the matrices from the atomic orbital (AO) basis to the molecular orbital (MO) basis. The spin coordinates of the electrons can be represented in terms of quaternion algebra in the four-index transformation step which helps to go from complex four-component to a two-component quaternion form. Therefore, the MO coefficients become quaternion and can be represented in terms of real matrices [18, 19].

The generation of a two-component Hamiltonian from the parent four-component Hamiltonian is the most preferred choice for the purpose which includes the spin-orbit interaction with a lesser cost as compared to the four-component Hamiltonian. The central idea behind the generation of a two-component Hamiltonian is that it should reproduce the positive-energy spectrum of the parent Hamiltonian. Foldy and Wouthuysen proposed an idea to decouple the large and small component by a unitary transformation of the four-component Hamiltonian. Another well known approach is the elimination of the small component from the wavefunction. However, these two approaches can be shown to be equivalent [20]. The exact two-component approach (X2C) in the two-component framework is one such approach to reduce the computational scaling which uses elimination of the small component from the parent four-component Hamiltonian. The detailed description of the X2C approach including various other two-component methods can be found in Ref. [13, 21, 22].

Over the years, the equation-of-motion coupled-cluster (EOMCC) method gained popularity among correlation methods for the treatment of electron correlation due to its simplicity and elegance. The idea of EOMCC [23, 24, 25, 26, 27, 28, 29, 30, 31] is conceptually very simple and it is operationally a two step process: (i) solution of coupled cluster problem with the N electron closed-shell determinant as reference and (ii) construction and diagonalization of the effective Hamiltonian matrix for the Fock-space sector of interest in the configuration space. It takes into account of both the dynamic and non dynamic part of the electron correlation. The exponential structure of the coupled cluster operator takes care of the dynamic part of the electron correlation and non dynamic part is included by means of diagonalization of the effective Hamiltonian matrix in the configurational space. The diagonalization of effective Hamiltonian, by and

large is associated with the multi-reference theories, whereas EOMCC works within a single reference description to tackle the complex multi-configurational wavefunction. Further, the relaxation effect, which has an important role in proper description of the eigenstates is also taken care. The multiple roots can be addressed in a single calculation and each of the states are treated with equal weightage. The EOMCC method behaves properly at the non-interacting limit but not rigorously extensive (only for the core-core and core-valence interactions) due to the linear structure of the EOM operator [32]. The EOMCC is in close kinship with the coupled cluster linear response theory (CCLRT) [33, 34] and symmetry adapted cluster expansion configuration interaction (SAC-CI) method [35, 36]. It is worth to note that the transition energy calculated using CCLRT is identical with the EOMCC method for the one valence problem but the transition moments is identical only when it is represented as a energy derivative in EOMCC framework. Chaudhuri *et al* [37, 38] applied relativistic CCLRT for the ionization problem of atomic systems with spherical implementation. Besides these two methods, effective Hamiltonian variant of Fock space multi-reference (FSMRCC) theory [39, 40, 41, 42, 43, 44] always comes in the discussion on EOMCC as these two methods produce identical results for the one valence problem. The amplitudes of all the lower sector including the sector of interest are involved in the FSMRCC theory. On the other hand, EOMCC deals with the amplitudes of the (0,0) sector and the sector of interest. Therefore, both the approaches are eventually produce the same result for the one electron attachment or detachment problem. The EOMCC is free from the problem of intruder due to its CI (configuration interaction method) like structure, which is associated with the effective Hamiltonian variant of the FSMRCC theory. There are ways in the FSMRCC framework to handle the problem of intruder such as the eigenvalue independent partitioning technique of Mukherjee (EIP-FSMRCC) [32, 45] and the intermediate Hamiltonian variant of the FSMRCC (IH-FSMRCC) theory [46, 47, 48].

Recently, Blundell implemented relativistic EOMCC method for the electron affinity problem and applied to calculate fine-structure splittings in high-lying states of rubidium atom [49]. The implemented version of Blundell is applicable only for the purpose of atomic calculations as they have used the spherical implementation which allows the separation of radial and angular parts. Therefore, the evaluation of radial in-

integrals is only required and the angular part will add up to it as a multiplier. The radial integrals can be evaluated numerically. Such a separation is not possible in molecular systems due to the absence of spherical symmetry. In our implemented version, we have used the one- and two- body matrix elements, which are evaluated in the Cartesian coordinate system. The Cartesian coordinate system does not allow one to exploit the spherical symmetry to separate the matrix elements into radial and angular parts. Furthermore, the anti-symmetrized two-body matrix elements are used in this coordinate system calculations, which is not possible in the spherical implementations as angular factor will be different for the direct and exchange part of the two body matrix element. Thus, our implemented version is a general one, applicable to both atoms as well as molecules starting from their closed-shell reference state configuration. It should be noted that the spherical implementation is much more complex than that of the molecular calculations, but it is favorable from the computational point of view as it requires only the solution of radial integrals. Therefore, atomic calculations are computationally easy, which allows to correlate more number of electrons and amenable to use huge basis for the correlation calculation to achieve a better accuracy.

In our recent work, the performance of the fully four-component EOMCC has already been established for both atomic and molecular systems for the single ionization and double ionization problem [50, 51, 52]. Therefore, in this article, we focus on the implementation of relativistic EOMCC method for the electron affinity problem applicable to both atomic and molecular systems. The implemented EA-EOMCC method is employed to calculate ionization potential of open-shell atomic systems starting from their singly positive closed-shell configuration. Further, the vertical EA values of molecular systems are also calculated. Both four-component and exact two component (X2C) calculations are done for all the considered systems. The effect of spin-orbit interaction is shown for the atomic systems in the EOMCC framework.

The manuscript is organized as follows. The EOMCC theory in regard to the electron attachment problem is briefly described in Sec. 2 and the computational details of our calculations are presented in Sec. 3. We have discussed our results in Sec. 4 and finally made concluding remarks in Sec. 5. We are consistent with the atomic unit if not stated explicitly.

2. Theory

In the EOMCC method the k^{th} target excited state of single electron attached state is defined as

$$|\Psi_k\rangle = R_k^{N+1}|\Psi_0\rangle, k = 1, 2, \dots \quad (1)$$

Here, the R_k^{N+1} is a linear operator, which on acting on the single reference coupled cluster (SRCC) ground state wave function $|\Psi_0\rangle$, generates the k^{th} excited state wave function $|\Psi_k\rangle$. The R_k^{N+1} operator takes the form in the coupled cluster single-double (CCSD) approximation as

$$\begin{aligned} R_k^{N+1} &= R_1 + R_2 \\ &= \sum_a r_a a_a^\dagger + \sum_{b < a} \sum_j r_j^{ba} a_a^\dagger a_b^\dagger a_j \end{aligned} \quad (2)$$

The R_1 and R_2 operator are diagrammatically represented in Fig. 1. The R_1 is a one particle (1p) creation operator and R_2 is a two-particle and one-hole (2p-1h) creation operator. The circled arrow is just to represent that overall it is a one electron attachment process.

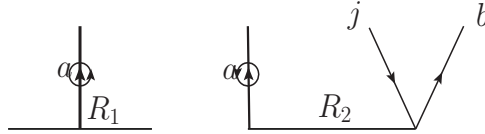


Figure 1: Diagrammatic representation of R_1 and R_2 operator.

The Schrödinger equation for the ground state ($k=0$) is

$$H_N|\Psi_0\rangle = \Delta E_0|\Psi_0\rangle, \quad (3)$$

The electron attached states ($k=1,2,\dots$) is written as

$$H_N R_k |\Psi_0\rangle = \Delta E_k R_k |\Psi_0\rangle \quad (4)$$

The above equation on multiplication with a non-singular operator e^{-T} (where T is the coupled cluster excitation operator) in the course it is assumed that R_k commute

with T (as strings of same quasi-particle creation operator) with some mathematical manipulation leads to equation of motion with respect to the R_k operator,

$$[\bar{H}_N, R_k]|\Phi_0\rangle = \Delta E_k R_k|\Phi_0\rangle \quad \forall k. \quad (5)$$

In the above equation, ΔE_k is the energy change associated with the electron attachment process and $\bar{H}_N = e^{-T} H e^T - \langle \Phi_0 | e^{-T} H e^T | \Phi_0 \rangle$ is the similarity transformed normal ordered effective Hamiltonian. In our case it is the Dirac-Coulomb Hamiltonian, which is given by

$$\begin{aligned} \hat{H}_{DC} &= \hat{H}_D + \sum_{i>j} \frac{1}{r_{ij}} \mathbb{1}_4 \\ &= \sum_A \sum_i [c(\vec{\alpha} \cdot \vec{p})_i + (\beta - \mathbb{1}_4)c^2 + V_{iA}] + \sum_{i>j} \frac{1}{r_{ij}} \mathbb{1}_4, \end{aligned} \quad (6)$$

where α_i and β are the usual Dirac matrices, V_{iA} is the nuclear potential and $\frac{1}{r_{ij}}$ is the electron-electron repulsion potential. The orbital energies are scaled with respect to the free electron rest mass energy (c^2), which is zero in the non-relativistic case. We have chosen a correlated determinantal space of $|\Phi^a\rangle$ and $|\Phi_j^{ab}\rangle$ (1p and 2p-1h) with respect to the Dirac-Hartree-Fock determinant ($|\Phi_0\rangle$) to project the above equation to get the desired electron affinity values, ΔE_k .

$$\langle \Phi^a | [\bar{H}_N, R_k] | \Phi_0 \rangle = \Delta E_k R^a, \quad (7)$$

$$\langle \Phi_j^{ab} | [\bar{H}_N, R_k] | \Phi_0 \rangle = \Delta E_k R_j^{ba}, \quad (8)$$

In Figs. 2 and 3, the contributing diagrams for the 1p and 2p-1h space is presented, respectively. The evaluation of these diagrams requires the solution of the coupled-cluster amplitude equations. The converged T_1 and T_2 amplitudes are contracted with the two-body matrix elements of the Hamiltonian matrix to construct one body, two body and three body intermediate diagrams. The intermediate diagrams are categorized into \bar{f}_{pp} , \bar{f}_{hp} , \bar{f}_{hh} , \bar{V}_{hppp} , \bar{V}_{pppp} , \bar{V}_{phph} , \bar{V}_{ppph} and \bar{W} . Here \bar{f} 's, \bar{V} 's and \bar{W} stands for one-body, two-body, and three-body intermediates, respectively. We have followed a recursive intermediate factorization scheme as described in Ref. [53] to evaluate these intermediate diagrams. The factorization scheme in the construction of intermediate

diagrams saves enormous computational resources. The matrix elements corresponding to the three-body intermediate diagram are not stored rather computed on the fly. The programmable algebraic expression for the diagrams corresponding to the projection of Hamiltonian to 1p and 2p-1h excited determinantal space are presented in Eq. 9 and 10, respectively. We have used the standard notation ($\bar{f}(\text{out}, \text{in})$) and (\bar{V} (left out, right out, left in, right in)) for one-body and two-body intermediate matrix element. In Eqn 9 and 10, $i, j, \dots (a, b, \dots)$ stands for hole (particle) index. \hat{P} is a permutation operator and any odd permutation introduces a negative sign. The Davidson algorithm [54] is implemented to get the desired set of eigenvalues and eigenvectors.

$$\Delta E_k R^a = \sum_b \bar{f}_{pp}(a, b) r^b + \sum_{j,b} \bar{f}_{hp}(j, b) r_j^{ba} + 0.5 \sum_{j,b,c} \bar{V}_{hpp}(j, a, b, c) r_j^{bc} \quad \forall a \quad (9)$$

$$\begin{aligned} \Delta E_k R_j^{ba} = & \hat{P}(ab) \sum_c \bar{f}_{pp}(b, c) r_i^{ca} - \sum_j \bar{f}_{hh}(j, i) r_j^{ba} + 0.5 \sum_{c,d} \bar{V}_{pppp}(a, b, c, d) r_i^{dc} \\ & - \hat{P}(ab) \sum_{c,k} \bar{V}_{phph}(a, k, c, i) r_k^{bc} + \sum_c \bar{V}_{ppph}(a, b, c, j) r^c \\ & - 0.5 \sum_{k,l,c,d} V_{hhpp}(k, l, c, d) r_k^{cd} t_{lj}^{ab} \quad \forall (i, b < a) \quad (10) \end{aligned}$$

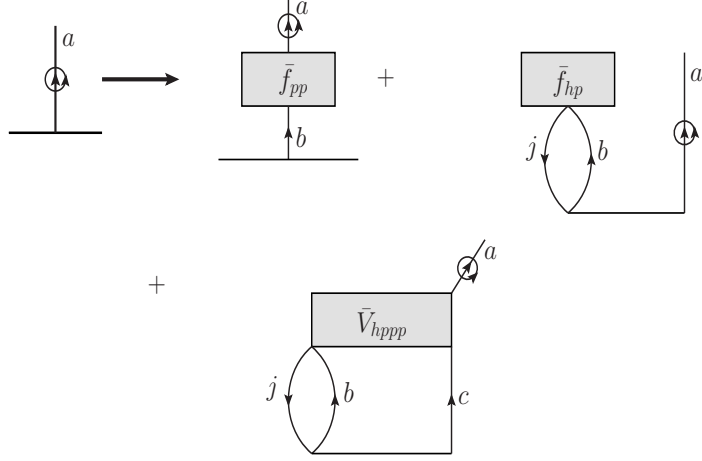


Figure 2: Diagrams contributing to the 1p block.

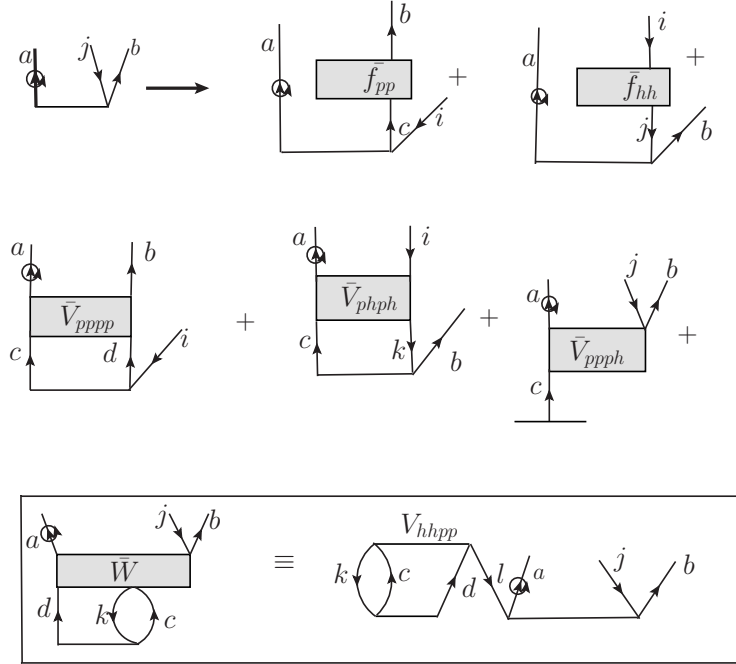


Figure 3: Diagrams contributing to the 2p-1h block.

Table 1: SCF (E_{DF}^0) and correlation energy from MBPT(2) and CCSD of alkali metal ions.

Atom	X2C			4C		
	SCF	MBPT(2)	CCSD	SCF	MBPT(2)	CCSD
Li ⁺	−7.237045	−0.038520	−0.042313	−7.237174	−0.038490	−0.042284
Na ⁺	−161.885871	−0.352072	−0.355824	−161.895637	−0.351504	−0.355258
K ⁺	−601.317915	−0.655371	−0.669654	−601.378197	−0.654132	−0.668419
Rb ⁺	−2979.125369	−1.603877	−1.544953	−2979.693217	−1.600533	−1.541667
Cs ⁺	−7784.579785	−1.746204	−1.654556	−7786.643511	−1.740037	−1.648569
Fr ⁺	−24296.910671	−1.635291	−1.468312	−24308.061505	−1.634768	−1.467783

Table 2: Bond length(in \AA), SCF (E_{DF}^0) and correlation energy from MBPT(2) and CCSD of LiX(X=H, F, Cl, Br) and NaY(H, F, Cl).

Molecule	Bond Length [55]	X2C			4C		
		SCF	MBPT(2)	CCSD	SCF	MBPT(2)	CCSD
LiH	1.5957	-7.987794	-0.069223	-0.080955	-7.987928	-0.069191	-0.080923
LiF	1.5939	-107.078887	-0.400341	-0.399171	-107.084024	-0.400097	-0.398927
LiCl	2.0207	-468.469738	-0.606016	-0.622235	-468.511539	-0.605515	-0.621738
LiBr	2.1704	-2612.134924	-1.465099	-1.404927	-2612.603993	-1.463721	-1.403588
NaH	1.8874	-162.602176	-0.385821	-0.397925	-162.611952	-0.385251	-0.397357
NaF	1.9259	-261.676902	-0.694456	-0.691459	-261.691677	-0.694011	-0.691018
NaCl	2.3608	-623.077913	-0.846128	-0.861815	-623.129354	-0.845488	-0.861179

3. Computational Details

The DIRAC program package [56, 57] is used to evaluate the required one-body and two-body matrix elements for the correlation calculation. Both the X2C and four-component calculations are done by using uncontracted finite atomic basis, which consists of scalar real gaussian functions. The small component of the basis is linked with the large component of the basis through the restricted kinetic balance (RKB) condition. The RKB condition represents the kinetic energy properly in the non relativistic limit and avoids the variational collapse [58]. This is achieved by pre-projecting in scalar basis and unphysical solutions are removed by diagonalizing the free particle Hamiltonian. The RKB condition generates the positronic solution and electronic solution in 1:1 manner. The DIRAC program package uses Gaussian distribution nuclear model to take care of the finite size of the nucleus. The used nuclear parameters are taken as default values from DIRAC package [59]. We adopted aug-cc-pCVQZ basis for Li^+ [60] and Na^+ [61] atom and all the generated orbitals are taken into consideration for the correlation calculations. Dyall.cv4z [62] basis is opted for K^+ and Rb^+ . We have neglected the virtual orbitals those energy is more than 500 a.u. for the K^+ and Rb^+ atom. The Cs^+ and Fr^+ are calculated using dyall.cv3z basis [62]. The cutoff used for Cs^+ atom is 1000 a.u. whereas for Fr^+ atom, we have taken the orbitals having energy in between -25 a.u. to 100 a.u. in our correlation calculations. In the molecular calculations of LiF, LiCl, LiBr, we have chosen aug-cc-pCVTZ basis for Li atom [60] and cutoff of 100 a.u. for the virtual orbitals. The calculations of F and Cl are done using aug-cc-pCVQZ [60, 61] basis and for Br, dyall.cv4z [64] basis is used. In LiH we have chosen aug-cc-pCVQZ basis [60] for Li and aug-cc-pVTZ [60] for the H atom and none of the electrons are frozen for the correlation calculations. Aug-cc-pCVTZ basis is opted for both Na [61] and Cl [65] in the calculations of NaCl and a cutoff of 100 a.u. is used for the virtual orbitals. The single particle orbitals and two-body matrix elements are generated by taking account of C_{2v} symmetry. Both X2C and four-component calculations of Rb and LiBr are done with the DIRAC14 version and rest of the calculations are done using DIRAC10. The implemented version of X2C SCF [66] in DIRAC10 is capable of taking up to g harmonics but the opted basis

Table 3: Convergence pattern of electron affinity (in eV) of the C_2 ($R=1.243 \text{ \AA}$, Ref [55]) as a function of basis set.

Basis	Spinor	Electron affinity	Expt.[63]
cc-pVDZ	88	2.6494	
cc-pCVDZ	104	2.6645	
aug-cc-pVDZ	124	3.1896	
aug-cc-pCVDZ	140	3.1949	
cc-pVTZ	152	3.1140	
cc-pCVTZ	192	3.1285	
aug-cc-pVTZ	216	3.3316	3.30 ± 0.1
cc-pVQZ	252	3.2743	
aug-cc-pCVTZ	256	3.3412	
cc-pCVQZ	316	3.2851	
aug-cc-pCVQZ	416	3.3840	
aug-cc-pCVQZ ^a	488	3.3853	

^a All the virtual orbitals are used for the EOMCC calculation.

for Rb and LiBr require up to h harmonics to express the large component of the wave function. Therefore, these two calculations are done using DIRAC14 version. We have fixed a cutoff of 10^{-12} to store the matrix elements for the intermediate diagrams as two-body matrix elements contributed negligibly beyond this limit. The convergence of 10^{-9} is fixed for the solution of SRCC amplitude equations and 10^{-5} for the Davidson algorithm in the EOMCC part. A direct inversion in the iterative subspace (DIIS) of 6 is used in the solution of ground state amplitudes for all the calculations. The newly implemented relativistic EOMCC code is tested by comparing EA-EOMCC results with the (1,0) sector FSMRCC code implemented in the DIRAC package as these two theories are supposed to produce identical results for one electron attachment process. The MBPT(2) correlation energy is identical whereas CCSD correlation energy

Table 4: Ionization potential values (in eV) of alkali metal atoms.

Atom	X2C	4C	NIST [67]
Li	5.3894	5.3895	5.3917
Na	5.1104	5.1106	5.1391
K	4.3419	4.3423	4.3407
Rb	4.1750	4.1756	4.1771
Cs	3.8861	3.8872	3.8939
Fr	4.0579	4.0603	4.0727

and the EA value are matching upto ten-digit and eight-digit, respectively. The test is performed with identical convergence cut off, equal number of DIIS space and without any cutoff in the intermediate diagrams. We have done the test over a series of atoms and molecules with various basis sets and successful in achieving similar agreement for all the considered system, independent of the choice of basis set.

4. Results and discussion

We have reserved this section of our manuscript to present numerical results of our calculations and to interpret the outcome of these calculations. The four-component and exact two component (X2C) EOMCC calculations are performed for all the considered atomic and molecular systems starting from their closed-shell configuration.

In Tables 1 and 2, we present numerical results of our SCF and correlation energy from MBPT(2) and CCSD calculation of singly positive alkali metal atomic systems (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Fr^+) and molecular systems (LiX ($\text{X}=\text{H}, \text{F}, \text{Cl}, \text{Br}$) and NaY ($\text{Y}=\text{H}, \text{F}, \text{Cl}$)) in their closed-shell configuration. The bond length of the molecular systems is also compiled in Table 2. For atomic systems (Table 1), we noticed that the difference between MBPT(2) and CCSD correlation energies for both X2C and four component calculation keep on increasing as we go down the group. This trend is expected as the effect of correlation increases as the number of electron in the system increases.

Table 5: Relative energy difference (in eV) of energy levels of atoms

Atom	2S	$^2P_{1/2}$			$^2P_{3/2}$			$^2P_{3/2} - ^2P_{1/2}$		
		X2C	4C	NIST [67]	X2C	4C	NIST [67]	X2C	4C	NIST [67]
Li	0.0000	1.8494	1.8495	1.8478	1.8495	1.8495	1.8479	0.0001	0.0000	0.0001
Na	0.0000	2.0837	2.0840	2.1023	2.0859	2.0862	2.1044	0.0022	0.0022	0.0021
K	0.0000	1.6128	1.6132	1.6100	1.6203	1.6206	1.6171	0.0075	0.0074	0.0071
Rb	0.0000	1.5610	1.5616	1.5596	1.5909	1.5915	1.5890	0.0299	0.0299	0.0294
Cs	0.0000	1.3912	1.3921	1.3859	1.4600	1.4609	1.4546	0.0688	0.0688	0.0687
Fr	0.0000	1.5198	1.5220	1.5172	1.7276	1.7298	1.7264	0.2078	0.2078	0.2092

We have done a series of calculations to understand how the electron affinity value changes with the nature of basis set and cutoff in the orbital energies can be used without losing considerable amount of accuracy as EOMCC calculations for the EA problem are computationally costly. We have chosen C_2 as an example system for which experimental vertical EA value is reported in the literature. We have started our calculation with cc-pVDZ, which is a very small basis as it generates only 88 spinor for the beyond SCF calculations using a cutoff of 100 a.u. for the virtual orbitals. A few more calculations are also done by improving the nature of the basis functions. The EA value as well as the number of generated spinor in different basis are tabulated in Table 3. We have taken 1.243 Å as bond length for the C_2 molecule, which is the experimentally reported bond length [55]. The reported experimental value is 3.30 ± 0.1 eV [63], whereas our calculation yields 3.3840 eV for aug-cc-pCVQZ basis with a cutoff of 100 a.u. in the virtual orbital energy. On the other hand, without using any cut off, the result is 3.3853 eV. Therefore, a cutoff of 100 a.u. for virtual orbital energies and similar basis set can be used without losing much accuracy for all other calculations to achieve a good agreement with the experiment. It will save enormous computational time without losing a significant amount of accuracy as contribution from the high energy virtual orbitals is very less in the correlation calculations. The reported experimental uncertainty is in the first digit after the decimal point. Therefore, it is hard to comment on the accuracy of our calculated results. It can be said that our results are also spanning same range starting from a reasonable basis. In Table 4, we report the calculated ionization potential values of atomic systems using both X2C and four-component EA-EOMCC method. We have started our calculations from singly positive alkali metal ions and applied EA-EOMCC method. The negative of the computed values are reported as ionization potential values of the open-shell atomic systems. These computed ionization potential values are compared with the values from the National Institute of Standards and Technology (NIST) database. A nice agreement with NIST values is achieved for all the considered systems. The maximum deviation is obtained for the Na atom, which is also in the accuracy of $\sim 0.6\%$ with the NIST value. The difference between the X2C with four-component results is in the fifth digit after the decimal for Li atom whereas the difference is about 0.01 eV for Fr

Table 6: Vertical EA (in eV) values of LiX (X=H, F, Cl, Br) and NaY (Y=H, F, Cl).

Molecule	X2C	4C	Others [68]
LiH	0.2968	0.2968	0.247
LiF	0.3550	0.3550	0.340
LiCl	0.5526	0.5526	0.551
LiBr	0.6148	0.6148	
NaH	0.3218	0.3217	0.319
NaF	0.4848	0.4849	0.485
NaCl	0.6726	0.6727	0.672

atom.

We have calculated electron attachment energy to the $p_{1/2}$ and $p_{3/2}$ orbitals of the atomic systems in the X2C and four-component EOMCC framework and presented as a relative energy difference with respect to the 2S states. These results are compared with the values from NIST database and presented in the Table 5. The results of our calculations are found to be very accurate with respect to the NIST values. It is interesting to note that the energy gap between the $p_{1/2}$ and $p_{3/2}$ is negligible for the Li atom but it keeps on increasing as the system size become heavier. This can be explained by the fact that the effect of relativity increases with the increase in atomic number and thus, the spin-orbit coupling plays a significant role in heavier systems.

In Table 6, we present the results of our calculations of vertical EA of molecular systems using both X2C EA-EOMCC and four-component EA-EOMCC method. Further, we have compared our result with the theoretical results calculated by Gutsev *et al* [68]. They also employed EA-EOMCC method for correlation treatment to calculate the vertical EA values of the molecular systems. In their calculation, Gutsev *et al* misses the effect of relativity, which is included in our calculation in its four-component formalism. We have achieved a nice agreement for the atomic results and also for the vertical EA value of C_2 molecule. Therefore, it can be said that our calculated results for the molecular systems are also quite accurate though there is no reliable experimen-

tal data or any other values calculated using any variant of relativistic coupled cluster theory to compare with. However, the accuracy of the molecular calculations will not be that much accurate as compared to the atomic results. The reason behind this is due to the possibility of structural change on attachment of an extra electron to the neutral molecule depending on the polarity of the molecule.

5. Conclusion

The relativistic EOMCC method for the electron attachment problem applicable to both atomic and molecular systems is successfully implemented. To test the performance of the EA-EOMCC method, we applied to calculate ionization potential values of alkali metal atoms starting from closed-shell configuration. We have compared our calculated ionization potential values with the values from NIST database. We are successful in achieving less than 1% agreement with the NIST values. We have also presented molecular EA values of LiX (X=H, F, Cl, Br) and NaY (Y=H, F, Cl) using our relativistic EOMCC methods.

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